(c) Composite Materials

by

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INTRODUCTION

A composite is a combined material created by synthetic assembly of two or more components - a selected filler or a reinforcing agent and a compatible binder (i.e., a resin) in order to obtain specific characteristics and properties [1]. Methodologies of composite fabrication and the resulting properties are described in detail in a number of comprehensive works, such as those of Lubin [1], Grayson [2], and the ASM International Handbook [3]. Moreover, the chemical and physical properties of the resins, reinforcement fibres and fillers are delineated both as individual components and in the finished material. The composite materials in this chapter, for the most part, consist of fiber reinforced resins and are frequently called reinforced plastics (RP or FRP).

The primary reinforcements used in the production of composites are glass, carbon/graphite, polyamide, cellulosic and other natural fibers. The most widely used reinforcement is glass fibre. When very high stiffness and strength are required, graphite and para-aramide (a type of polyamide) are often used. The configuration of the fiber reinforcement in the resin may be as continuous or chopped strands, woven fabric, swirl mats or various combinations of the same.

The resin matrix used in composites consists of thermosetting or thermoplastic polymers. Typical resins include polyester, polyimide, polycarbonate, polyethylene, polypropylene, polystyrene, fluorocarbon polymers, acrylonitrile-butadiene-styrene terpolymer, alkyd, epoxy, melamine, and silicones [3]. Although polyester resins combined with glass fibers are the most widely used composite, epoxy resin composite dominates the aircraft/aerospace structural applications. Other resins, such as polyimides, are more expensive and less widely used than the polyesters and epoxy resins, but are preferred when optimal thermal stability at high temperature is required.

Composite materials offer advantages over metal, for some applications, in weight savings, corrosion resistance, and nonmagnetic character. But the resin in all composites is organic and may increase the risk of fire. For several years, researchers at NIST have been studying the flammability problems of composites, in order to help the U.S. Navy arrive at design criteria. It is seen that the use of fiber-reinforced resins on board naval ships will be dramatically increasing in the coming years; this growth of usage must necessarily be accompanied by a careful strategy for fire-safe performance.

A literature survey [4] indicated that older test types were not appropriate for determining actual performance of composites; thus the focus came to be on HRR and other modern methods. A few studies have been completed on the LIFT apparatus [5],[6], but most of the work has centered on using the Cone Calorimeter [7], [8].

TYPES OF COMPOSITES

The materials whose HRR properties have been studied so far are listed in Table 1. These were chosen primarily because of potential applicability to shipboard use, although certain other materials were included for a comparative basis. For the most part, only the generic classification of the resin and a general classification of the fiber reinforcement were known. Where greater detail of the materials is available, this is indicated in the results section. The generic classification of the resin and fiber identification were provided by the makers, as indicated. The resin classifications are epoxy, polyester, bismaleimide (BMI), and poly(phenyl sulfide) (PPS). In general, the resin reinforcement was a glass fiber fabric except for the Ryton PPS panels and panels prepared in the laboratory in which carbon fibers were used.

Table 1
Composite Materials

Material	Resin classification	Fiber reinforcement	Source
Koppers Dion Panels	Polyester, brominated	Glass woven roving	Koppers Co., Inc.
Corflex Panel Assembly	Epoxy filled with aluminium silicate	Glass	Corflex Corp per DTRC
Ryton Panels	Poly(phenylene sulphide)	Glass/graphite	Phillips Petroleum Co.
Lab. Panels	Epoxy	Graphite	DTRC
Lab. Panels	BMI	Graphite	DTRC

The specimens were prepared at the standard 100 mm by 100 mm face size, and using the full thickness of the supplied product. The testing was in accordance to ASTM E 1354.

IGNITION AND TIME DEPENDENT HEAT RELEASE RATE

Ignition

The first performance aspect to be examined was the resistance of materials to piloted ignition under radiative heating. The times to ignition are shown in Table 2. The trends of the data can better be seen from log-log plots of the data. Figure 1 shows the results for the Koppers Dion 6692T panel (25 mm thick) and the Corflex panel (3 mm thick). Linear regression lines for the data points show slopes of -2.3 and -1.7, respectively, for the Koppers and Corflex panels. Table 3 lists the slopes for all remaining composites.

As indicated in Chapter 9(b), the negative slope, in the simplest case, would be 2.0 for thermally thick materials, 1.0 for thermally thin ones, and on the order of 1.5 for intermediate cases. This does not appear to hold for the present data on composite panels. While the value of 2.3 for the 25 mm thick Koppers panel is certainly close to the thermally thick theoretical value of 2.0, the other data are more difficult to explain. The 3 mm Corflex panel and the 3.2 mm Ryton panels have nearly the same thickness, yet significantly different slopes. The answer, presumably, lies in the fact that these **are**, in fact, composite materials. Thus, the theoretical model, developed for homogeneous substances, could well be expected

Table 2
Ignition Delay Times (s) for Composite Materials Exposed to Various External Flux Levels

Material (thickness)	Incident flux (kW/m^2):			
	25	35	50	75
Koppers 6692T (25 mm)	263	120 (10)[a]	60 (2)	21
Corflex panel (3 mm)	—	92 (5)	54 (2)	25
Corflex assembly (37 mm)	—	122	70 (0)	30 (2)
Ryton panels (3 mm):				
glass mat (chopped)	—	183 [b]	66	27 (2)
glass woven mat prepreg	—	154 (7)	75	29 (1)
Lab. epoxy panel (3 mm)	—	116	76	40
Lab. BMI panels (3 mm)	—	211	126	54

[a] Numbers in parentheses indicate range about a mean of duplicate measurements made.
[b] Duplicate tests performed; only one specimen ignited.

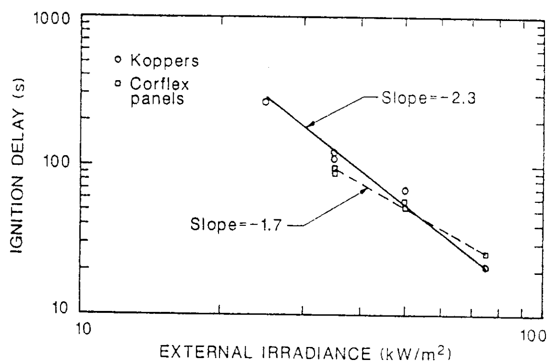

Figure 1. Time to ignition as a function of irradiance, shown for two different composites

not to apply. Unfortunately the thermal properties of these composites are not known well enough at elevated temperatures, and so a more refined analysis is not made.

Plotting ignition-delay data for all Cone Calorimeter experiments allows one to extrapolate the regression line to some chosen location. Extrapolation to 600 s represents a rough estimate of the critical flux needed for ignition. The study was not carried out in sufficient detail needed to arrive at a true value of this critical flux for ignition. Instead, values are listed in Table 3 for some intermediate times, 300 s and 600 s. The minimum external radiant fluxes required to attain ignition at those two times are listed as $MERF_{300}$ and $MERF_{600}$.

Table 3

Minimum External Flux for Long Exposure Time and for 300 s Exposure to Cause Ignition Computed from the Regression of Ignition Delay Time and External Flux

Material	Regression slope	$MERF_{600}$[a] (kW/m^2)	$MERF_{300}$[b] (kW/m^2)
Koppers 6692T (25 mm)	–2.3	18	24
Corflex panel (3 mm)	–1.7	12	18
Corflex assembly (37 mm)	–1.9	15	22
Ryton panels (3.2 mm):			
glass mat (chopped)	–2.5	21	28
glass mat (swirl)	–2.6	23	31
glass woven mat prepreg	–2.1	18	25

[a] Minimum external radiant flux necessary to cause ignition after 600 s exposure.
[b] Minimum external radiant flux necessary to cause ignition after 300 s exposure.

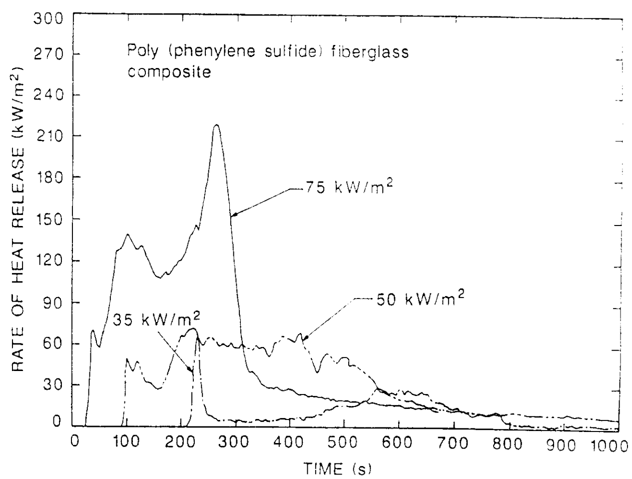

Figure 2. Example of the effect of irradiance on the heat release rate

Heat Release Rate

We next consider the Cone Calorimeter results for HRR for these same materials. It was found that, due to the complex nature of the material and its pyrolysis, the HRR curves obtained presented some unique traits. The HRR curves, of course, depend both on the chemical composition of the resin and on the thickness of the composites. Figure 2 shows the HRR of 3 mm thick PPS/glass fiber (Ryton) panels, subjected to irradiances of 35, 50, and 75 kW/m^2. These curves demonstrate typical variations observed in the HRR-time profiles of composites panels.

In general, all of the curves exhibit at least two maxima for HRR. The initial peak is due to surface volatilization, which then reduces due to char formation. The second peak is a result of an increase in the gasification rate of the unburned substrate caused by an increase in the bulk temperature of the substrate. The bulk temperature increases because the unburned substrate is no longer thermally thick. Back surface temperatures should increase as the second peak of HRR is approached. While these measurements were not made in this investigation, the studies on wood (another char-former), considered in the previous Chapter, show the same phenomenon.

In most cases the HRR changes quite significantly with time, so it appears that more meaningful information may be gained about the fire behavior of the composites under radiative heating if the rates of heat release are averaged over periods of time during the burning process. Not only are the advantages of curve smoothing brought forward to clarify trends in the heat release data, but such averaged data are often better predictors of full-scale performance than is the

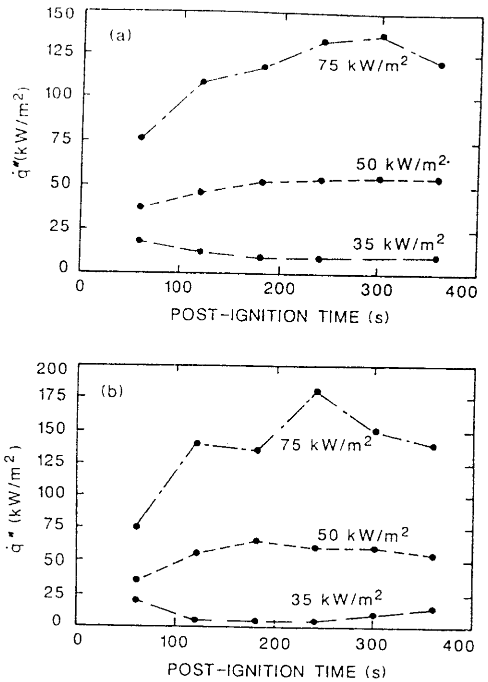

Figure 3. (a) Average $\dot{q}''$ for 3 mm Ryton panels, shown for progressively longer averaging periods (b) The average $\dot{q}''$ values, plotted for the previous 1-min intervals at each given point

peak of the curve (e.g., see the Chapter 14 of upholstered furniture). Kanury and Martin [9] also have used average values for deducing physicochemical properties of essentially homogeneous materials in fire environments. ASTM E 1354 specifies that average $\dot{q}''$ values for the first 60, 180, and 300 s after ignition be included in the report of the Cone Calorimeter results. Here, we will tabulate data also at all other 1-min intervals.

Figure 3 illustrates the behavior of the averaged HRR of the Ryton composite. This composite shows the greatest sensitivity to irradiance level. The effect of irregular volatilization of fuel from the surface is reduced. The lowest irradiance level, 35 kW/m^2, as was seen in the ignition data, provides barely enough energy to promote combustion. On the other hand, the average HRR at irradiances of 50 and 75 kW/m^2 increases until 300 and 240 s, respectively, when the panels are burned out. Table 4 summarizes the average HRR of the Ryton (PPS) panels. We note that ignition did not occur in one specimen reinforced by a chopped mat of glass fibers. Overall, the HRR at the 35 kW/m^2 flux level is low, always less than the irradiance.

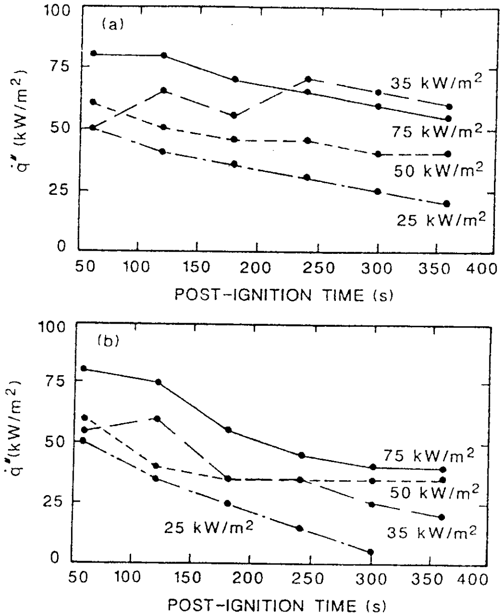

Figure 4. (a) Average $\dot{q}''$ for Koppers (FR polyester/glass) panels, shown for progressively longer averaging periods (b) The average $\dot{q}''$ values, plotted for the previous 1-min intervals at each given point

Figure 4 shows a plot of the average HRR for 25 mm thick polyester (Koppers) panels, exposed to four flux levels. In this case, the effect of the flux level on the average HRR values is smaller, presumably due to the greater material thickness.

Table 5 summarizes the results obtained for the 25 mm thick Koppers polyester composite. The $\dot{q}''$ value averaged at 60 s for one of the specimens tested at 35 kW/m^2 appears to be larger than expected. An explanation for this behavior is not known.

Next, the average $\dot{q}''$ values are summarized for two epoxy resin composites. The average $\dot{q}''$ values of a fire retardant epoxy are listed in Table 6. Interestingly enough, comparative data for 37 mm thick panels (not shown) are very similar during the initial burning period to those shown for the 3 mm panels.

The average $\dot{q}''$ results for the second resin type, a high performance experimental epoxy resin composite are shown in Table 7. Although the exact composition of the experimental resin is not known other than it being an amine-cured epoxy resin, it appears that its fire performance closely resembles that of the FR epoxy composite shown in Table 6. The average $\dot{q}''$ results of another experimental 3 mm panel composite, prepared from a bismaleimide (BMI) and graphite fibers are listed in Table 8.

Table 4
Results of Post-ignition Averaging of the Rate of Heat Release of 3 mm Thick Ryton Panels (Reinforced Poly(phenylene sulfide))

Fiber reinforcement	Flux (kW/m^2)	Average rate of heat release (kW/m^2)					
		60 s	120 s	180 s	240 s	300 s	360 s
Chopped mat	35	50	30 (10)[a]	20 (5)	20 (10)	20 (20)	20 (25)
		NI	—	—	—	—	—
	50	75	65 (60)	70 (75)	85 (135)	90 (105)	80 (30)
	75	110	115	130	130	115	100
	75	100	95 (95)	105 (125)	120 (155)	110 (75)	100 (45)
Woven mat	35	10	5	<5	<5	<5	<5
	35	5	5	<5	<5	<5	<5
	50	35	45 (60)	50 (64)	55 (95)	55 (110)	55 (45)
	75	85	90	95	100	95	80
	75	80	85 (85)	90 (110)	95 (110)	90 (60)	80 (25)

[a] Values in parentheses are single-minute averages, ending at the indicated time.
NI — no ignition during a 600 s exposure.

Table 5
Results of Averaging the Rate of Heat Release of 25 mm (1 in) Koppers Dion 6692T Panels (FR Polyester/Glass Fiber Composite)

Flux (kW/m^2)	Average rate of heat release (kW/m^2)					
	60 s	120 s	180 s	240 s	300 s	360 s
25	50	40 (35)[a]	35 (25)	30 (5)	25 (5)	20 (<5)
35	55	65 (60)	55 (40)	70 (35)	65 (25)	60 (20)
35	70	55	45	40	40	35 (25)
50	60	50 (40)	45 (35)	45 (35)	40 (35)	40 (35)
50	60	45 (35)	40 (35)	35 (25)	35 (25)	20 (25)
75	80	80 (75)	70 (55)	65 (40)	60 (40)	55 (40)

[a] Values in parentheses are single-minute averages, ending at the indicated time.

Table 6
Average Rate of Heat Release of 3 mm Corflex Panels (FR Epoxy–Fiberglass Composites)

Flux (kW/m^2)	Average rate of heat release (kW/m^2)					
	60 s	120 s	180 s	240 s	300 s	360 s
35	170	155 (140)[a]	160 (175)	140 (7)	—	—
35	170	170 (170)	160 (145)	130 (30)	105 (15)	90 (10)
50	175	190 (205)	155 (90)	120 (20)	100 (10)	—
50	175	180 (185)	180 (180)	145 (45)	120 (20)	105
75	215	215 (215)	165 (75)	130 (25)	—	—

[a] Values in parentheses are single-minute averages, ending at the indicated time.

Table 7
Average Rates of Heat Release of 3 mm Laboratory Samples of Epoxy–Graphite Fiber Composite Panels

Flux (kW/m^2)	Average rate of heat release (kW/m^2)					
	60 s	120 s	180 s	240 s	300 s	360 s
35	150 (160)[a]	155 (50)	120 (20)	95 (≈0)	75	—
50	185 (155)	170 (60)	135 (15)	105 (10)	85 (10)	75
75	210	190	145	150	100	—

[a] Values in parentheses are single-minute averages, ending at the indicated time.

Table 8
Results of Post-ignition Averaging of the Rate of Heat Release of a 3 mm Thick Laboratory Sample of BMI–Graphite Fibers Composite

Experiment number	Flux (kW/m^2)	Average rate of heat release (kW/m^2)					
		60 s	120 s	180 s	240 s	300 s	360 s
2296	35	105	130 (130)[a]	135 (140)	120 (90)	105 (40)	90 (10)
2308	50	120	145 (170)	145 (150)	130 (90)	110 (35)	96 (15)
2313	75	140	170 (200)	165 (133)	145 (75)	125 (30)	105 (25)

[a] Values in parentheses are single-minute averages, ending at the indicated time.
NI — no ignition during a 600 s exposure.

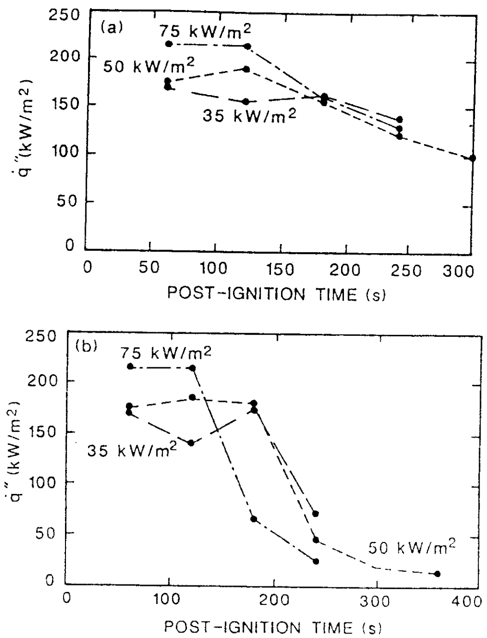

Figure 5. (a) Average $\dot{q}''$ for 3 mm Corlex (FR epoxy/glass) panels, shown for progressively longer averaging periods (b) The average $\dot{q}''$ values, plotted for the previous 1-min intervals at each given point

It may be seen in reviewing the average $\dot{q}''$ data in Tables 4-8 that the composites with polyester and epoxy resins generally show maximum $\dot{q}''(t)$ values in the first 60 s post ignition. The $\dot{q}''(t)$ values generally decrease with time after the first 60 s which suggest that the peak HRR is associated with initial surface burning of the composite rather than subsequent combustion of the pyrolysate from the interior of the composite. For irradiances of 50 kW/m^2 or more, the composites with PPS and BMI resins show maxima at times greater than 60 s. For these samples, the maximum $\dot{q}''(t)$ is not the initial peak.

PREDICTIVE ASPECTS OF HEAT RELEASE RATES

Analysis Based on Effective Heat of Gasification

Proceeding in a manner similar to Kanury and Martin [9] and Kanury [10], it is possible to express the HRR as

$$\dot{q}'' = \frac{\Delta h_{c,eff}}{L}\,[\dot{q}_T'' + \dot{q}_e'' + \dot{q}_l''] \qquad (1)$$

where

$\Delta H_{c,eff}$ = effective heat of combustion
L = heat of gasification (pyrolysis)
$\dot{q}_T''$ = heat transferred from flame to material surface
$\dot{q}_e''$ = imposed external flux
$\dot{q}_l''$ = heat flux loss by the surface to ambient

The slope ($\Delta H_{c,eff}/L$) of a plot of the measured HRR against the external radiant flux can be taken to provide a measure of the flammability of materials, it is termed the thermal sensitivity index (TSI) [9], provides a basis by which the fire performance of the materials may be indexed and compared over a broad range of external irradiances, simulating different fire environments. The intercept of such a plot indicates, in principle at least, whether the flame is self-sustaining in the absence of an external radiant flux for the time period under consideration. We will call this parameter the extinction sensitivity index (ESI); Kanury and Martin [9] called this parameter the limiting thermal index. Equation 1 then becomes,

$$\dot{q}'' = (\mathrm{TSI})\dot{q}_e'' + (\mathrm{ESI}) \qquad (2)$$

We illustrate the dependence of the average HRR with respect to imposed heat flux levels by plotting the average $\dot{q}''$ at 60 s versus external flux, $\dot{q}_e''$. Using 60 s average $\dot{q}''$ minimizes the effect of sample thickness and conductive heat losses. Figure 6 shows the results for composites whose resins are polyester, FR epoxy, PPS and BMI. This plot illustrates the dependence of the TSI and ESI on the resin composition.

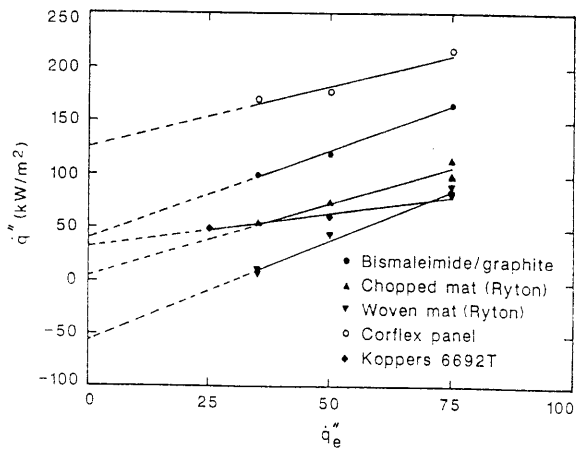

Figure 6. The HRR (average for the period of 60 s after ignition) for several composites, shown as a function of irradiance

Table 9 summarizes the slopes, intercepts, average effective heat of combustion. The ESI values (slopes) are estimates of the sensitivity of the combustion intensity to variations in external irradiance and show that the Koppers composite, Corflex Panel Assembly, and BMI Panel had about the same sensitivity to variations in $\dot{q}''_e$. Because of differences in sample thickness these samples should not be compared to each other without caution. However, the TSI values indicate that the rate of heat release of these samples, although not the same in magnitude, would be fairly insensitive to small changes in external irradiance. This suggests that in a real fire the decay in an external fire imposing energy on a target material made from one of these composites would not be reflected as rapidly in a reduced heat release rate of the target material as compared to the materials with higher TSI values. For example, the Ryton Panels, which ranged in value from 1.3 to 1.8, would be expected to respond most strongly to variations in source irradiance.

The Ryton Panels also exhibited a negative intercept, ESI. This suggests that the heat loss from the flame is greater than its flux to the surface. With the removal of an external heat source these materials can be expected to self-extinguish, while the other materials with a positive ESI would be expected to continue burning at least for the first 60 s. The intercepts indicate that the epoxy matrix composite exhibits the most potential for sustained combustion with an external radiant flux following ignition.

In Table 9, the effective heat of combustion values are averages taken from each exposure over the entire measurement; they are computed from the ratio of $\dot{q}''$ to mass loss rate, $\dot{m}''$. These values fall into two groups, the lower one (about

Table 9
Comparison of Inferred Flamability Indices of Composite Materials

	$\Delta H_{c,eff}$ (kW/m^2)	TSI[a]	ESI[b] (kW/m^2)
Koppers Dion 6692T (25 mm)	12±2	0.6	30
Corflex panel (3 mm)	12±0.9	1.1	125
Corflex panel assembly (3 mm)	12±0.4	0.6	100
Lab. epoxy panel (3 mm)	20	1.4	100
Lab. BMI panel (3 mm)	20	0.9	75
Ryton panels (3 mm)			
chopped mat	25±1.6	1.3	5
swirl mat	22±2.0	1.6	–55
woven mat	23±2.2	1.8	–40
graphite woven mat	23±0.03	1.6	—
average	23±1.3	1.6±0.20	—

[a] TSI — thermal sensitivity index.
[b] ESI — extinction sensitivity index.

12 kJ/g) where the resin is flame retarded and the upper values (20-25 kJ/g) where it is unretarded.

At the moment there are no full-scale data available for composites of the kind examined here. It is expected, however, that within the next few years full-scale data will begin to be available. At that point it will be possible to no longer deal in hypothetical predictors, such as TSI and ESI, but, rather, to develop predictive techniques which are validated against the bench scale results.

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